# BIOMASS GASIFICATION FOR HYDROGEN PRODUCTION – PROCESS DESCRIPTION AND RESEARCH NEEDS

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#### INTRODUCTION

Renewable biomass and biomass-derived fuels could be readily gasified to produce a hydrogen-rich gas or hydrogen. Among the biomass energy conversion schemes gasification produces a product gas, which based on its properties could be used either to co-produce value-added byproducts or hydrogen. As a readily renewable fuel, biomass may become a significant component in the global sustainable energy mix as fossil fuel resources begin to deplete. In addition, biomass utilization can expedite mitigation of greenhouse gas emissions and carbon sequestration cycles and promote "green" industries with associated growth in rural economies. Hydrogen or hydrogen-rich gas produced from biomass could be readily used in most of the present natural gas or petroleum derived hydrogen energy conversion devices and also in advanced systems such as fuel cells.

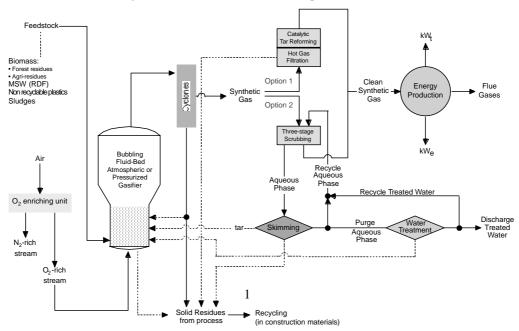
### **Process Descriptions**

At present, there are no commercial biomass gasification processes for hydrogen production. In general, except for direct air-blown gasification, enriched-air or oxygen-blown gasification, steam gasification, or any other indirectly heated gasification process should be able to produce a synthesis gas, which could be converted to hydrogen. From the wide variety of biomass gasification processes that are being developed, processes considered to be suitable for hydrogen production are described in the following sections.

BIOSYN Gasification and Gas Conditioning Technologies: The BIOSYN gasification process (Figure 1) was developed during the 1980s by BIOSYN Inc., a subsidiary of Nouveler Inc., a division of Hydro-Quebec (Montréal, Quebec, Canada). The process is based on a bubbling fluidized bed gasifier containing a bed of silica or alumina capable of operating up to 1.6 MPa. Extensive oxygen-blown biomass gasification tests were conducted during 1984 to 1988, in a 10 TPH demonstration plant located at St-Juste de Bretennieres, Québec, Canada, to produce synthesis gas for methanol production. Air blown atmospheric gasification tests were also conducted for evaluating cogeneration. In the following years, a 50kg/h BIOSYN process development unit has also proven the feasibility of gasifying primary sludges, RDF, rubber residues (containing 5 - 15% Kevlar), and granulated polyethylene and propylene residues.

The process accepts feed particle sizes up to 5 cm, feed bulk densities higher than 0.2 kg/l and feed moisture content up to 20%. The thermal efficiency for biomass gasification varies from 70 to 80%. The product gas containing mostly CO, CO<sub>2</sub>, and H<sub>2</sub> could be cleaned to remove carry over dust and condensable tar and upgraded to produce essentially pure hydrogen. With air as the gasifying agent the HHV of the fuel gas is about  $6 \text{ MJ/Nm}^3$ . Enriched air, with 40% oxygen, can produce a fuel gas having a HHV of about  $12 \text{ MJ/Nm}^3$  at half the gas yield. The raw gas cyclones remove 85 to 95% of entrained particles.

# The BIOSYN Options for Waste & Biomass Gasification & Synthetic Gas Conditioning



#### Figure 1

The supporting R& D conducted during the demonstration of the BIOSYN Process, includes gas scrubbing for efficient tar removal with reduced water requirements, recycling the insoluble tars to the gasifier, wet oxidation and adsorption of dissolved organic compounds in the scrubbing water, and recycling carbon-rich ashes and carry over carbon with adsorbed organic compounds to the gasifier. The R& D effort also includes hot-gas filtration of entrained dust using a static bed of perlite particles and a moving sand bed filter, and catalytic steam cracking of tar. Proprietary catalysts were developed to decompose 99% of tars and 97% of naphthalene compounds. The BIOSYN Process fully integrated with hot-gas filtration and high-temperature tar removal, and gas processing to convert CO to hydrogen and CO<sub>2</sub>, and CO<sub>2</sub> removal to produce pure hydrogen was never demonstrated. The BIOSYN Process is commercialized by Enerkem Technologies Inc, a subsidiary of the Kemestrie Group, a spin-off company of the University of Sherbrooke. Recently, a commercial installation to gasify 2.2 TPH of granulated polypropylene residues was planned for construction in Spain. Environmental International Engineering S.L., a Spanish-based development and engineering group, in partnership with Enerkem, was planning to erect and commission the plant. The electricity output of the plant will be sold to the grid.

FERCO SilvaGas Process: The FERCO SilvaGas Process (Figure 2) employs the low-pressure Battelle (Columbus) gasification process which consists of two physically separate reactors; a gasification reactor in which the biomass is converted into a MCV gas and residual char at a temperature of 850° to 1000°C, and a combustion reactor that burns the residual char to provide heat for gasification. Heat transfer between reactors is accomplished by ciculating sand between the gasifier and combustor. Since the gasification reactions are supported by indirect heating, the primary fuel gas is a medium calorific value fuel gas. A typical product gas composition obtained in pilot plant tests, at steam to biomass (wood chips) ratio of 0.45, is 21.22% H<sub>2</sub>, 43.17% CO, 13.46% CO<sub>2</sub>, 15.83% CH<sub>4</sub>, and 5.47% C2+. The estimated HHV of this fuel gas is 17.75 MJ/N cu.m. A 200 TPD capacity Battelle demonstration gasification plant was built at the McNeil Power plant in Burlington, Vermont. Following plant shakedown and initial tests the plant has been operating intermittently. During the first phase the fuel gas will be cofired in the existing McNeil boiler. In subsequent phases, the fuel gas will be cooled for heat recovery, scrubbed, and recompressed prior to energy conversion and recovery in a 15MWe gas turbine system. The process was developed by US DOE Biomass Power Program, FERCO, Battelle Columbus Laboratory, Burlington Electric Department, Zurn Industries, OEC/Zurn, and NREL.

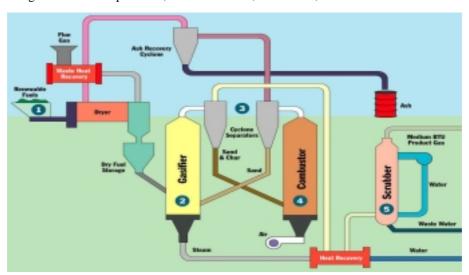


Figure 2. SilvaGas Process

MTCI Process: The MTCI gasification process (Figure 3) also employs indirect heating to promote steam gasification of biomass to produce a MCV fuel gas. The gasifier combusts part of the fuel gas in pulsed combustion burners which promote heat transfer to the gasification section. Extensive pilot plant tests were conducted in a 20 TPD PDU at MTCI laboratories near Baltimore, Maryland. These tests also included an evaluation of black liquor gasification. Based on the PDU tests a 50 TPD capacity black liquor gasification demonstration unit was built at Weyerhauser's New Bern facility. The MTCI process group is currently designing and building a modular system and also seeking partnerships and support to demonstrate other gasification applications.

Since, the MTCI Process employs indirect heat transfer, it has the capability to produce synthesis gas, rich in CO and  $H_2$ , from biomass. At present the primary focus is to develop the technology for black liquor gasification. Efforts are underway to design the system for high-temperature operation to improve carbon conversion to desirable product gases and to develop the appropriate materials and engineering designs to handle corrosive characteristics of black liquor.

Georgia Pacific, Fluor Daniels, and Stone Chem, the MTCI technology provider with support from USDOE is constructing a 200 TPD sodium carbonate black liquor gasification demonstration plant at the Big Island, Virginia GP paper mill. The five-year demonstration project, which was started in February 2001, will cost about \$87 MM with about 50% cost contribution from industry.

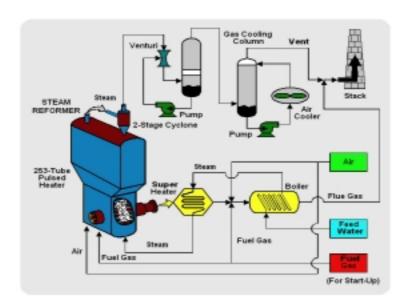


Figure 3. MTCI Process (Schematic for Pulse Heater Qualification Tests)

In the MTCI Process, the black liquor is steam reformed/gasified at an operating temperature of about 600°C (~1,110°F). The raw gas is upgraded through several steps of gas cleanup, resulting in a synthesis gas rich in hydrogen (>65% by volume) with a higher heating value (HHV) of approximately 10.4 MJ/m³ dry (280 Btu per dry scf). The cleaned synthesis gas was metered to an SOFC, operating at about 1000°C (1,830°F), which produced a net 2.6 volts D.C., 62 amps or an equivalent of 161 watts of "green" power.

RENUGAS Process: The GTI/IGT RENUGAS process (Figure 4) employs a 20 bar pressurized bubbling fluidized bed process. The process was extensively tested with a variety of biomass materials, including bark-sludge mixtures, bagasse, and pelletized alfalfa stems in a 12 TPD PDU at IGT test facilities in Chicago. Subsequently USDOE selected the IGT process for scale-up and demonstration, using bagasse, at the HC&S sugar mill at Paia in Hawaii. Since, this 100 TPD demonstration plant had limited success in handling the low-density, shredded bagasse the project was terminated. A typical gas composition obtained in the IGT PDU with bagasse at 2.24 MPa, and 850°C is 19%H<sub>2</sub>, 26% CO, 37%CO<sub>2</sub>, 17% CH<sub>4</sub>, and 1% C2+. The heating value of this fuel gas is approximately 13 MJ/Nm³. The project participants included US DOE Biomass Power Program, IGT, Westinghouse Electric Corporation, State of Hawaii, PICHTR, and HC&S.

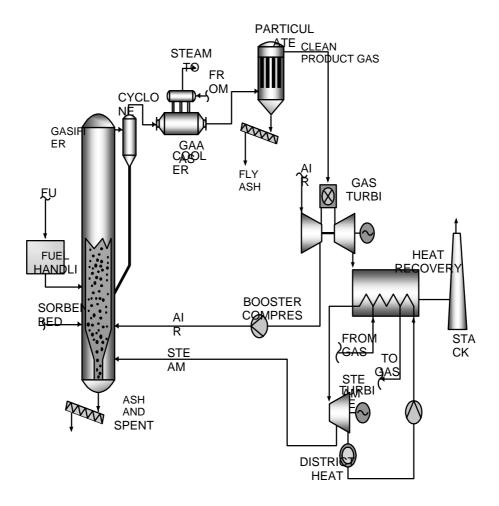


Figure 4. RENUGAS Process

The pressurized RENUGAS process coupled with hot-gas particulate and alkali cleanup is ideally suited for IGCC applications and to generate electricity at efficiencies in the 40 to 42% range. IGT is currently seeking partnerships and support for further demonstration of the RENUGAS process.

<u>Fast Internal Circulation Fluidized Bed (FICFB) Process</u>: The FICFB gasification reactor (Figure 5) consists of two zones, a gasification zone and a combustion zone. Inert, heat carrying bed material is circulated between these two zones to transfer heat from the combustion zone to the gasification zone, while separating the flue gases in the combustion zone from the fuel gas produced in the gasification zone. Biomass is fed into the gasification zone and gasified with steam at 850-900°C and the thermal energy provided by the circulating solids. As a result the gas produced in this zone is nearly free of nitrogen. The bed material, together with the char left over from steam gasification, is circulated to the combustion zone. This zone is fluidized with air to burn the char and any carryover interstitial fuel gas. The product gas produced from the steam gasification zone is a medium calorific value (MCV) synthesis gas rich in hydrogen. There is no need for pure oxygen to produce the MCV gas in this process.

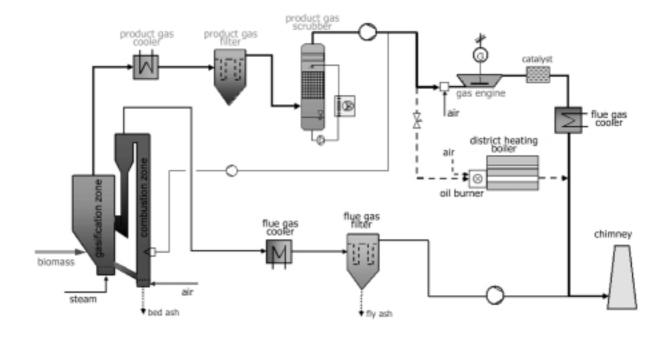


Figure 5. FICFB Gasification Process

Following the initial development of the FICFB Process in a laboratory test unit at Technical University of Vienna (TUV), a demonstration plant was erected. This plant is a 8MWth feed capacity plant situated in Güssing, Burgenland with an electric output of 2MW. The plant went into operation in Autumn 2001. A typical dry, raw gas composition reported from air-blown biomass gasification tests is given below:

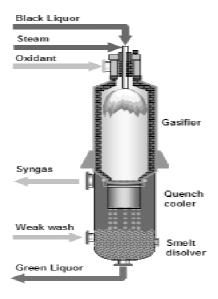
Hydrogen	30-45 vol.%
Carbon monoxide	20-30 vol.%
Carbon dioxide	15-25 vol.%
Methane	8-12 vol.%
Ammonia	500-1000 ppm
Nitrogen	1-5 vol.%
Hydrogen sulfide	20-50 ppm
Tar	0,5-1,5 g/Nm³
Particles	10-20 g/Nm <sup>3</sup>

Characteristic data of the demonstration plant are:

Type of plant	Demonstration plant	
Fuel Power	8000	kW
Electrical output	2000	kW
Thermal output	4500	kW
Electrical efficiency	25,0	%
Thermal efficiency	56,3	%
Total efficiency	81,3	%

CHEMREC Process: Kvaerner started the development of the Chemrec Process (Figure 6) or black liquor gasification in 1987, in Sweden (IEA,1997). The gasification reactor part is similar to the TEXACO gasification process. A slurry of black liquor is injected with steam and a preheated oxidant, into a high-pressure ( $\sim$  32 bar) and high temperature ( $\sim$ 950°C) reactor to gasify the cellulose and lignin components. In the air-blown Chemrec process, black liquor is introduced with preheated air at 500°C. Atomization and droplet size are very important to gasifier performance; atomization is achieved using medium pressure steam. The injection nozzles are designed to facilitate on-line cleaning. The gasifier temperature is controlled by air injection rate, typically with an airflow of 40-50% of stoichiometric combustion air. The reactor temperature is maintained at about 950°C in the lower part of the gasifier. An air burner at the top of gasifier is used to heat the gasifier for start-up and to

prevent interruption in feed. The chemical smelt is recovered from the gas stream at the base of the gasifier by quenching with green/weak liquor. The product green liquor is pumped to the mill system. The final smelt recovery and  $H_2S$  removal from the product fuel gas are accomplished by a combination venturi scrubber and spray/packed bed scrubber. The weak liquor is injected in the venturi scrubber to remove particulates from the product gas before entering the spray scrubber. The absorption of  $CO_2$  from the fuel gas is reduced by maintaining a low gas temperature and controlling the pH of the weak wash liquor. With air gasification, the higher heating value of the product gas is  $3.2 - 3.7 \, \text{MJ/m}^3$ .



**Figure 6: Chemrec Process** 

No data was available from the manufacturer on the composition of the fuel gas from the Chemrec, air-blown, low-pressure gasification process. However, it will be similar to the gascomposition for pressurized gasifiers, as predicted by Consonni et al, 1998, based on a complex heat and mass balance model that assumes chemical equilibrium conversion of the black liquor. The estimated higher heating value of the dry product gas from air-blown gasifier is about 4.1 MJ/m³, increasing to 9.1 MJ/m³ for the oxygen-blown gasifier.

Table 2-2 Gasifier Performance Predictions for Operation with Air and Oxygen

	High Pressure	***************************************	High Pressure
	Air Blown		Oxygen-blown
Assumptions:			
Reactor Temp, °C	950		1000
Reactor Pressure, bar	25		25
Air feed, t/tds	1.91		
O2 feed, t/tds			0.471
Oxidant temp, °C	390		135
Predicted Results:			
Raw gas yield t/tds	2.784		1.344
Composition (mol. %):			
Ar	0.55		0.87
$CH_4$	2.32		2.15
CO	10.53		23.06
$CO_2$	11.45		18.57
COS	0.03		0.05
$H_2$	10.31		22.37
$H_2O$	17.59		31.52
H2S	0.59		1.08
NH3	0.01		0.00
N2	46.62		0.32
Higher heating value			
(MJ/m3, dry, 15C)	3.4		6.3
Recovered compounds t/tds			
Na2SO4 (wt % in smelt) 0.004		0.002	
Na2CO3	79.945	79.525	
Na2S	8.00		7.901
NaOH	1.61		2.119

K2CO3	9.63	9.645
K2SO4	0.005	0.002
C	0.805	0.806

BL properties: C 37.2%, H 3.6%, O 34.4%, S 3.7%, N 0, Na 18.6%, K 2.5%

HHV: 14.36 MJ/kg, dry NAV: 12.409 MJ/kg, dry Source: Consonni, et al, 1998

The Chemrec process is under review to resolve problems with the reactor refractory. Besides materials, other problems to date have included plugged spray quench nozzles, air blower outages, black liquor pump seal and refractory failures. Currently the refractory is expected to last less than one year. Other improvements are needed to operate at 100% of the gasifier's maximum continuous rating, optimize the quench and scrubber performance and improve the reliability of the power boiler and condensing heat exchanger. The recovery of H<sub>2</sub>S selectively in the scrubber also needs improvement. The Swedish Government is providing \$25 MM to develop and verify the performance of the Chemrec process in a 20 TPD dry solids (3 MWth) pilot unit at Pitea in Sweden and to scale-up the process to a 300 TPD dry solids at a location that is yet to be selected. This effort, which began in 2001, will continue through 2006. Upon completing the 20 TPD pilot tests, Weyerhaeuser and US DOE will consider building a commercial Chemrec plant in USA for black liquor gasification and chemical recovery.

#### **SVZ Schwarze Pumpe GmbH:**

SVZ has converted some of the existing former East German era coal gasifiers in Schwarze Pumpe, Germany to convert biomass, coals, and wastes into clean fuel gas and synthesis gas (Figures 7a, 7b, 7c). The plant gasifies a wide variety of waste materials along with low-rank coals. The waste materials include demolition wood, used plastics, sewage sludge, auto-fluff, MSW, contaminated waste oil, paint and varnish sludge, mixed solvents, tars, and on-site process waste streams. The waste materials are blended with coal at a ratio of 4:1. SVZ has developed an effective feed handling and feed preparation system that combines heterogeneous feed materials to prepare a nearly uniform gasifier feed.

The oxygen-blown, 25 bar-pressurized, 14 TPH FDV process, similar to Lurgi's moving bed coal gasification process, converts the mixed feed stocks to MCV fuel gas or synthesis gas. The raw gas is subject to conventional gas cleaning to separate contaminants from the product gas.

The oxygen-blown, 25 bar pressurized, 35 TPH British Gas Slagging Lurgi gasifier system installed at this facility also converts the mixed feed stocks to MCV fuel gas or synthesis gas. As is the case with the FDV process, the raw gas is subject to conventional gas cleaning to produce a clean product gas and liquid and solid slurry waste stream.

The third oxygen-blown gasifier is the FSV 15 TPH entrained flow gasifier, similar to the TEXACO process, which serves the role of a "bottoming" gasifier that effectively treats the hydrocarbons containing waste streams from gas processing into a contaminant-free synthesis gas and mineral slag. If required, a supplementary fuel, i.e. natural gas is used to maintain the reactor temperature in the range of 1600°C.

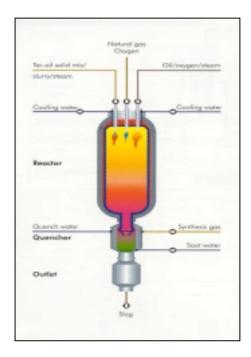
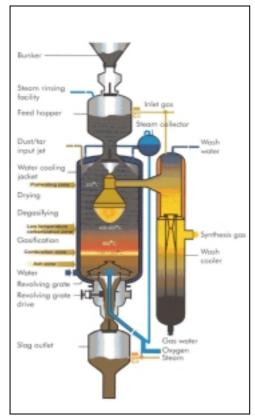


Figure 7A. SVZ Schwarze Pumpe Entrained Flow Gasfier



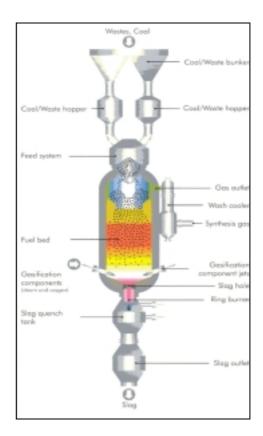


Figure 7B. Pressurized Solid Bed Gasifier with Revolving Grate

Figure 7C: Pressurized Solid Bed Gasifier with Liquid Slag Discharge

These three gasifiers operate in an integrated fashion to recover the carbon values from 30 TPH of waste materials and coal to produce synthesis gas that is now converted to methanol and co-produced combined-cycle electricity. If required, the plant design and operation could be modified to produce pure hydrogen.

The SVZ plant is a first-of-a-kind integrated gasification, methanol and combined-cycle electricity production plant that converts contaminated and difficult to handle waste materials to clean, value-added products. The high gasification temperatures of up to 1,800°C are high enough to significantly reduce contaminants in the product gas or gas scrubbing effluent streams. The vitrified slag, the only gasifier waste product, safely encloses any residual pollutants and can be used as construction material.

## RESEARCH NEEDS

The following sections highlight research needs for developing and commercializing biomass gasifiers for hydrogen production. The general issues relateto hydrogen handling. Compression, storage and transportation are not discussed.

<u>Feed Preparation:</u> Unlike fossil fuels, biomass is dispersed and lacks the infrastructure to ensure sustained supply of low-cost quality controlled gasification feedstock. Biomass has certain physical characteristics, such as low bulk density and its fibrous nature that presents many challenges in collection and transportation to a central gasification plant. Although, woody biomass feed preparation and feed handling systems are well developed for low-pressure systems, reliable feeders for many varieties of biomass for pressurized gasifiers are required. Low-cost pelletization of low-density herbaceous feed stocks would widen the range of renewable feed materials that are available for biomass gasification. Pellets are easy and economical to transport and their relatively uniform shape and bulk density would render them easy to handle, store and feed pressurized systems.

Biomass Gasification: The present gasification systems are generally designed and operated to produce fuel gas for heat and power. The processes described above also produce a fuel gas with little or no inert N2, i.e., produce a synthesis gas containing primarily CO,  $H_2$ ,  $CO_2$ ,  $H_2O(g)$ , and some gaseous hydrocarbons and condensable hydrocarbons. Fundamental research is needed to improve product selectivity, to produce essentially  $H_2$ ,  $CO_2$ , and  $H_2O$ . The role of catalytic and non-catalytic bed additives on raw product gas yield and thermodynamic limitations should be investigated. Nearly total carbon conversion to produce such a raw gas containing  $H_2$ ,  $CO_2$ ,

and  $H_2O$  would require minimal gas cleaning and separation to produce pure  $H_2$ . It is conceivable that direct  $H_2$  could be increased by varying certain aspects of gasification reactor designs and operating conditions. Gasification reactors should also be designed to incorporate the capability to thermally decompose organic condensates and ammonia that would be produced from systems employing conventional low-temperature gas cleaning and quenching.

Robust and sturdy low-cost, high-temperature heat transfer materials, which can operate up to 1100°C (~2000°F) would help develop indirect heating reactor designs that would prevent products of combustion from contaminating steam- or 'recycled product gas-' gasification of biomass.

Small-scale, low-cost air enrichment is another technology that will be beneficial to hydrogen production by biomass gasification.

Raw Gas Handling and Clean-up: Significant progress has been made over the past 10 years towards developing a better understanding of biomass gas handling and conditioning processes and technologies for use in biomass gasification for advanced power production. However, there is need for further R&D in this process step for removal or elimination of particulates (from attrition of gasifier solids and secondary vapor-phase carbonaceous materials), alkali compounds, tar, chlorides, and ammonia. High-temperature gas processing, including reforming of hydrocarbons and water-gas shift to convert CO to H<sub>2</sub> should be investigated, particularly for raw product gases with all its contaminants produced in biomass gasification. In order to improve the overall thermal efficiency and to retain process simplicity, it is desirable to conduct these gas cleaning at raw gas temperatures or at temperatures which may require some gas cooling but does not require any reheating of raw cleaning gases. Gas cooling and design of appropriate heat exchangers have become the focus of the recent demonstration of the AMER and ARBRE biomass gasification projects, for co-firing and power generation applications. In the development of high-efficiency gasification systems, it may be necessary that most if not all of these gas handling and gas clean-up R&D should be conducted at elevated pressures that match with the end-use for product H<sub>2</sub>.

Gas cleaning R&D should also investigate  $CO_2$  removal at high temperatures, although it may not be required for biomass gasifiers that may be developed for MCFC. Physical and ionic separation membranes that can separate  $H_2$  at high temperatures would be useful to produce pure  $H_2$ , while CO or gaseous hydrocarbons are being chemically converted to  $H_2$ .

Gas cleaning in general will have a major impact on the environmental impact of biomass gasifiers. Incomplete gas cleaning would shift the contaminant removal problem downstream from the gasifier, requiring expensive treatment of all process effluents.

Interface Issues and System Integration: As is the case with other energy conversion schemes, there could be several unique issues that need to be addressed for integrating hydrogen producing biomass gasification systems with selected end use applications. Obviously a central hydrogen producing biomass gasifier or gasifiers feeding to a central hydrogen storage and distribution system may face simpler problems compared to hydrogen producing biomass gasifiers that are closely coupled to selected chemical or energy conversion systems. Examples of the latter include issues related to coupling gasifiers with high-temperature fuel cells.

System Definition and Market Assessment: Whenever, 'biomass gasification to hydrogen' becomes commercial, it would be necessary to determine the range of capacity of conceptual commercial plants. These specifications would be dependent to a great extent on the application, the cost and availability of feedstock. Upon defining the basic plant specifications, it would be possible to determine the process economics, their advantage over conventional alternatives, and hence the market potential for biomass gasifiers for specific applications.

<u>Information Dissemination and Policy:</u> To promote the successful development and commercialization of biomass gasifiers for hydrogen production and utilization, timely dissemination of information is absolutely essential. Given the competition from conventional sources of hydrogen, public education and information are definitely required to craft, deploy, and implement policies that are conducive to commercializing hydrogen producing biomass gasification systems. It is crucial to document the performance of the new biomass gasification systems, to highlight success stories but also in showing solutions to problems that may arise. The deployment of hydrogen producing biomass gasification systems for high-efficiency and selected value-added applications will benefit from policies that encourage the use of renewable fuels.

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